

UNCLASSIFIED

AD NUMBER

**AD367137**

CLASSIFICATION CHANGES

TO: **unclassified**

FROM: **confidential**

LIMITATION CHANGES

TO:

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FROM:

**Controlling DoD Organization. Director,  
Advanced Research Projects Agency, 1400  
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AUTHORITY

**30 Sep 1977, Group-4, DoDD 5200.10; 30 Sep  
1977, DoDD 5230.24**

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AD 367 137

ROCKETDYNE  
A DIVISION OF NORTH AMERICAN AVIATION, INC.  
6633 CANOGA AVENUE CANOGA PARK CALIFORNIA

R-5883-4

(Unclassified Title)

QUARTERLY PROGRESS REPORT,  
INORGANIC HALOGEN OXIDIZERS  
(29 May 1965 through 28 August 1965)

Group 4  
Downgraded at 3-Year Intervals  
Declassified After 12 Years

Contract Nonr 4428(00)

Sponsored by Advanced Research Projects Agency  
Washington 25, D. C.  
ARPA Order No. 23

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**FOREWORD**

The research reported herein was supported by the Advanced Research Projects Agency through the Office of Naval Research, Power Branch, Code 429, with Mr. Richard L. Hanson as Scientific Officer. This report was prepared in compliance with Section H of Nonr 4428(00) under ARPA Order No. 23, and covers the period 29 May 1965 through 28 August 1965. This work was carried out in the Synthetic Chemistry Group with Dr. D. Pilipovich, Principal Scientist of the Fluorine Chemistry Unit, as the Responsible Scientist. Full-time associates connected with the technical effort were Dr. H. F. Bauer, Dr. C. J. Schack, and Dr. C. B. Lindahl.

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**ABSTRACT**

The new oxidizer oxychlorine trifluoride,  $\text{ClF}_3\text{O}$ , has been prepared by the fluorination of cesium fluoride complexes of both chlorine monoxide and chlorine nitrate. The density of  $\text{ClF}_3\text{O}$  is 1.90  $\pm 0.05$  g/cc at 25.5 °C; it melts at -66 °C and boils at 29.4 °C. The vapor pressure/temperature equation for  $\text{ClF}_3\text{O}$  has been obtained from -22 to 32 °C:  $\log_{10} p \text{ (mm)} = 8.433 - 1680/T$ . The molar heat of vaporization is 7.7 kcal. Oxychlorine trifluoride was found to be thermally stable to 284 °C, although reactivity with metal containers was noted. Elemental analyses confirm the empirical formula  $\text{ClF}_3\text{O}$ .

Several members of a new class of complexes have been formed:  $\text{Cl}_2\text{O}\cdot\text{CsF}$ ,  $\text{Br}_2\text{O}\cdot\text{CsF}$ , and  $\text{ClONO}_2\cdot\text{CsF}$ . Fluorination of these materials has led to solid oxyhalogen fluoride complexes. Evidence for another new oxychlorine fluoride candidate has been obtained during this study.

Reactions of  $\text{ClF}_3\text{O}$  with Lewis acids and bases gave the complexes  $\text{NO}_2^+\text{ClF}_4\text{O}^-$ ,  $\text{Cs}^+\text{ClF}_4\text{O}^-$ ,  $\text{ClF}_2\text{O}^+\text{BF}_4^-$ , and  $\text{ClF}_2\text{O}^+\text{AsF}_6^-$ , indicating a pronounced amphoteric behavior. No reaction of  $\text{ClF}_3\text{O}$  was observed with either  $\text{F}_2$  or  $\text{N}_2\text{F}_4$ .

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A new, convenient synthesis of  $\text{Cl}_2\text{O}$  has yielded a product of improved purity. The reaction of  $\text{BrF}_5$  with  $\text{FOClO}_3$  failed to give  $\text{BrF}_6^+ \text{ClO}_4^-$  while the reaction of  $\text{Cl}_2\text{O}$  and  $\text{N}_2\text{F}_4$  gave no new products.

(Confidential Abstract)

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**INTRODUCTION**

During a search for new inorganic halogen oxidizers several avenues of interest have been explored, particularly those leading to new compounds containing fluorinated nitrogen, oxynitrogen, halogen, and oxyhalogen moieties. One of the primary objectives of this program, oxychlorine trifluoride, was achieved during last year's effort. This eagerly sought compound is the first known chlorine oxyfluoride containing but one chlorine-oxygen bond.

During the past quarter, effort has been directed primarily toward the elucidation of the synthesis and properties of oxychlorine trifluoride,  $\text{ClF}_3\text{O}$ . An understanding of the chemistry of this new compound has aided materially in the improvement of its synthesis as well as suggesting syntheses for the unknown, related compounds  $\text{ClFO}$  and  $\text{ClF}_5\text{O}$ .

Various aspects of the chemistry of chlorine monoxide, the principal source of  $\text{ClF}_3\text{O}$  to date, were fruitfully investigated. As a precursor to new  $\text{BrF}_x\text{O}$  oxidizers, bromine monoxide was studied in a parallel manner.

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**DISCUSSION**

**OXYCHLORINE TRIFLUORIDE ( $\text{ClF}_3\text{O}$ )**

The characterization of oxychlorine trifluoride has continued and satisfactory elemental analyses have been obtained. This new Cl, F, O compound has been studied with regard to new synthetic methods, improvement of the existing synthesis, thermal stability, and other physical characteristics. The physical properties presented in Table 1 are a summary of the best available data.

**TABLE 1**

**PROPERTIES OF OXYCHLORINE TRIFLUORIDE**

Melting Point, C (corrected)	-66 $\pm$ 1
Boiling Point, C	29.4 $\pm$ 1.0
Molecular Weight	
Found (vapor density)	105
Calculated	108.5
Solar Heat of Vaporization, kcal	7.7
Trouton Constant	25.4
Density, g/cc at 25.5 C	1.90 $\pm$ 0.05

The properties were measured from samples of oxychlorine trifluoride which was analyzed as follows: Cl, 30.8 percent; F, 49.5 percent; and O, 2.3 percent. The theorized analysis was Cl, 32.7 percent; F, 52.5 percent; and O, 14.7 percent.

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Physical Properties of ClF<sub>3</sub>O

Vapor Pressure/Temperature Relation. The vapor pressure/temperature equation of oxychlorine trifluoride was determined from -22°C to 32°C at nine temperatures. A least-squares fit yielded the equation  $\log_{10} p(\text{mm}) = 8.433 - 1680/T$ . The normal boiling point is 29.4°C and the heat of vaporization is 7.7 kcal/mole indicating a fairly associated liquid.

Density Measurements. The density of oxychlorine trifluoride was determined in two ways using a Kel-F pycnometer. A known volume of liquid was weighed and gave densities of 1.89 and 1.91 g/cc at 25.5 ± 1.0°C. The quantity of gas from a known liquid volume was determined and converted to ClF<sub>3</sub>O weight, using 108.5 as the molecular weight. This weight corresponded to a liquid density of 1.95 g/cc at 23°C and 2.06 g/cc at 18°C. The direct method not only gave more reproducible data than the gas volume method but allowed calculation of the sample purity by molecular weight as well (105 vs 108.5 theory). Insufficient data were obtained to establish a quantitative dependence of density on temperature.

Thermal Stability of Oxychlorine Trifluoride. Samples of ClF<sub>3</sub>O were heated in stainless steel and Monel for periods of 16 hours. Cesium fluoride was added to the stainless-steel cylinders. The runs in Monel were carried out in the presence and absence of fluorine. The data presented in Table 2 show the percent of ClF<sub>3</sub>O recovered.

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TABLE 2

THERMAL STABILITY OF  $\text{ClF}_3$

Container	Duration, hours	Temperature, C	Other Material Present	Recovery of $\text{ClF}_3$ , percent
Stainless Steel (five runs)	16	200	$\text{CsF}$	0
Monel	16	70	$\text{F}_2$	41
Monel	16	100	$\text{F}_2$	87
Monel	16	200	$\text{F}_2$	63
Monel	16	200	$\text{F}_2$	66
Monel	16	284	$\text{F}_2$	70
Monel	16	200	None	63
Monel	16	200	None	67

The absence of monotonic results indicates reaction with the container to be more important than thermal degradation. There was no evidence for equilibrium reactions involving  $\text{ClF}_3$ .

Elemental Analysis of Oxychlorine Trifluoride

The combustion of  $\text{ClF}_3$  and anhydrous ammonia in glass gave nonreproducible results. Metal-Teflon reactors were more successful and the following analytical results were obtained: Calculated for  $\text{ClF}_3$ : Cl, 32.7 percent; F, 52.5 percent; found: Cl, 30.8 percent; F, 49.5 percent. The low results were attributed to 88- and 94-percent material recovery based on initial  $\text{ClF}_3$  gas volumes. The fluorine-to-chlorine ratios for the recovered material were 2.97 and 2.99, respectively.

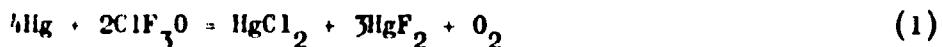
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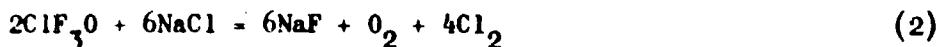


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The determination of oxygen in  $\text{ClF}_3\text{O}$  was attempted directly by the reaction:

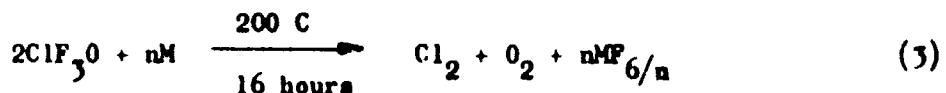


Incomplete oxygen release was observed so an indirect method was tried using sodium chloride:



Although the theoretical ratio of chlorine to oxygen was four, ratios from two to eight were obtained by gas/liquid chromatography. More satisfactory results were obtained when  $\text{NaCl}$  was reacted at 200 C and the oxygen volume was obtained by pumping the oxygen gas at -196 C with a Toepler pump. The following analytical results were obtained: calculated for  $\text{ClF}_3\text{O}$ : 0, 14.7 percent; found: 0, 12.3 percent.

Another method of chlorine and oxygen analysis became available when it was observed that oxychlorine trifluoride reacts with the inside surface of a stainless-steel cylinder at 200 C to give a gas mixture containing only chlorine and oxygen:



During four runs,  $\text{ClF}_3\text{O}$  was heated to 200 C in the presence of  $\text{CsF}$  for a minimum of 16 hours. The condensable gas was measured and compared to the amount of reacted  $\text{ClF}_3\text{O}$  on a molar basis.

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The following analytical results were obtained: calculated for  $\text{Cl}_2/\text{ClF}_3\text{O}$ : 0.50 percent; found: 0.50, 0.49, 0.48, and 0.49 mole percent.

The nature of the reaction was confirmed by mass spectrometric analysis of the volatile products of a fifth reaction:  $\text{Cl}_2$ , 59.9 m/o;  $\text{O}_2$ , 40.1 m/o. The relatively low oxygen content was not unexpected due to the possibility of oxide formation from  $\text{ClF}_3\text{O}$  at 200 C.

New Syntheses of Oxychlorine Trifluoride

Fluorination of Chlorine Nitrate. There are few well-characterized singly bonded chlorine-oxygen compounds represented by the structure  $\text{XOCl}$ . Because one of these, chlorine monoxide, proved successful in the preparation of  $\text{ClF}_3\text{O}$ , the possible utility of chlorine nitrate,  $\text{ClONO}_2$ , was examined. Low-temperature fluorinations of the cesium fluoride-chlorine nitrate complex were carried out in a fashion similar to the preparation of  $\text{ClF}_3\text{O}$  from  $\text{Cl}_2\text{O}$ . Chlorine nitrate was prepared by the reactions of  $\text{Cl}_2\text{O}$  with  $\text{N}_2\text{O}_4$  and with  $\text{N}_2\text{O}_5$  (Ref. 1).

On exposure of chlorine nitrate to cesium fluoride at -80 C, a slow lowering of vapor pressure was observed indicating some complex formation. The reaction was reversible because chlorine nitrate could be removed by warming and pumping. The  $\text{CsF-ClONO}_2$  complex was treated with excess fluorine at -80 C for several days.

After removal of excess fluorine at -196 C, the products volatile at ambient temperature were principally  $\text{FNO}_2$  and less  $\text{FClO}_2$  with one case of  $\text{HNO}_3$  and  $\text{N}_2\text{O}_5$  contamination. No further volatiles were evolved even after 4 weeks. Because not all of the starting material was accounted

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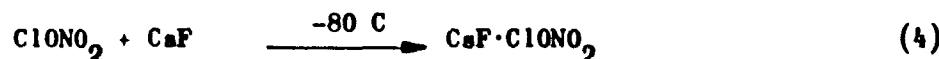
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for, the residues were heated to drive off any complexed ClF compounds in a manner analogous to that used for obtaining pure ClF<sub>3</sub> from KF-KClF<sub>4</sub> (Ref. 2). Colorless gases were evolved, containing 60- to 80-percent ClF<sub>3</sub>O with FN<sub>2</sub>, FC<sub>2</sub>O<sub>2</sub>, and ClF<sub>3</sub> comprising the remainder. The yield of ClF<sub>3</sub>O based on chlorine nitrate was 36 percent. Because the total product gases did not correspond to the initial amount of chlorine nitrate, additional unrecovered ClF<sub>3</sub>O may have been tied up in the solid, indicating the need for more drastic pyrolysis conditions. When the chlorine nitrate-cesium fluoride complex was formed at -18 C and treated similarly, a 22-percent yield of ClF<sub>3</sub>O was obtained.

The following reaction sequence is proposed:



Fluorination of Mercury Salt-Cl<sub>2</sub>O Complexes. The static method used for preparing Cl<sub>2</sub>O (discussed later in this report) indicated the formation of a complex between Cl<sub>2</sub>O and the residual mercury salts. A decrease in the vapor pressure of Cl<sub>2</sub>O was observed as well as incomplete Cl<sub>2</sub>O removal from the salts at -80 C. Proceeding by broad analogy with the CaF-Cl<sub>2</sub>O complex, the preparation of ClF<sub>3</sub>O or other new F, Cl, O moieties was attempted by fluorination.

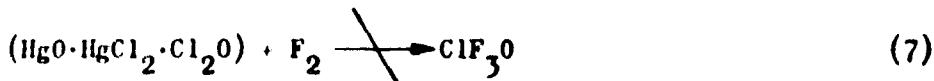
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Two reactions of this type were conducted at -80°C, but did not yield  $\text{ClF}_3^0$ :



Among the products obtained, however, were  $\text{FClO}_2$ ,  $\text{ClF}_3$ , and  $\text{ClF}_5$ . The observation of  $\text{ClF}_3$ , and  $\text{ClF}_5$  in particular, at this low temperature suggested a highly active form of chlorine because  $\text{ClF}_5$  had not been previously produced under such mild conditions. In addition, the infrared spectrum of the products contained several unidentified peaks. Attempts to separate and identify these products were unsuccessful.

#### A New Synthesis of $\text{Cl}_2^0$

Because of the increased requirements for  $\text{Cl}_2^0$  as an intermediate in several preparations essential to this work, an improved synthetic route was desired. The presently accepted, and indeed the only proved method of preparing  $\text{Cl}_2^0$  is via the ambient temperature flow reaction of nitrogen-diluted chlorine and freshly prepared yellow  $\text{HgO}$  (Ref. 3). This procedure is rather tedious and generally gives 85-percent  $\text{Cl}_2^0$  (15-percent  $\text{Cl}_2$ ) with 60- to 70-percent conversion of the  $\text{HgO}$  according to the following literature reaction.



It has been found that the static reaction of  $\text{HgO}$  and  $\text{Cl}_2$  at -80°C, using either the above stoichiometry or excess  $\text{HgO}$ , produces high-purity

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$\text{Cl}_2\text{O}$  in good yield with minimal effort. Furthermore, it has been established that under these conditions at least, the stoichiometry of the reactions approaches:



when the  $\text{Cl}_2:\text{HgO}$  ratio exceeds 2:1. The results from some representative preparations are presented in Tables 3 and 4. The  $\text{Cl}_2\text{O}$  yields are for purified material after removal of the  $\text{Cl}_2$  impurity.

TABLE 3

CONVERSION OF  $\text{Cl}_2$  TO  $\text{Cl}_2\text{O}$  BASED ON  $2\text{HgO} + 2\text{Cl}_2 = \text{Cl}_2\text{O} + \text{HgO}\cdot\text{HgCl}_2$   
(HgO IN EXCESS)

HgO: $\text{Cl}_2$ , mole ratio	HgO, millimoles	$\text{Cl}_2$ , millimoles	$\text{Cl}_2\text{O}$ Yield, percent
1:1	9.1	9.06	100
1.08:1	281.6	260.8	79
1.5:1	127.4	84.3	79
2:1	18.2	9.06	77
2:1	18.7	9.33	80
4:1	37.4	9.33	70

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TABLE 4

CONVERSION OF HgO TO Cl<sub>2</sub>O BASED ON HgO + 2Cl<sub>2</sub> = Cl<sub>2</sub>O + HgCl<sub>2</sub>  
(Cl<sub>2</sub> IN EXCESS)

HgO, millimoles	Cl <sub>2</sub> O, millimoles	Cl <sub>2</sub> O Yield, percent
169	119	70.4
229	129	56.3
277	225	81.2
233	187	80.2
193	184	95.5

Thus, the technique using excess chlorine gave maximum utilization of the HgO and achieved nearly quantitative conversion of the oxygen of HgO to Cl<sub>2</sub>O. Other pertinent advantages of this method were its simplicity and safer handling for gross quantities of the explosive Cl<sub>2</sub>O. Because the dispersed Cl<sub>2</sub>O was drawn off as required from the mercury salt-Cl<sub>2</sub>O reactor, the need to handle large volumes of liquid Cl<sub>2</sub>O was eliminated.

The exact mechanism by which Cl<sub>2</sub>O is formed from HgO and Cl<sub>2</sub> is not completely understood. It is known, however, that Cl<sub>2</sub>O was not all present as free material when in contact with the mercury salts at -80 C. This was demonstrated by the lower vapor pressure (2 millimeters) exhibited under these conditions than that shown by pure Cl<sub>2</sub>O (6 to 8 millimeters). Moreover, it was not possible to remove all the Cl<sub>2</sub>O by pumping on the mixture at -80 C. Only 50- to 60-percent was evolved at that temperature, the remainder being obtained on warming the reactor to ambient temperature. The possibility of a Cl<sub>2</sub>O-HgCl<sub>2</sub> complex is therefore being investigated.

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When part or all of the  $HgO$  was converted to  $HgCl_2$  by chlorine, an active form of  $HgCl_2$  was formed. Exposure of  $HgCl_2$  so formed to moist air resulted in a partial conversion to chlorine, mercuric oxide, and mercury.

Effect of Experimental Conditions on  
Oxychlorine Trifluoride Synthesis

One of the reaction sequences postulated for the conversion of  $Cl_2O$  to  $ClF_3O$  is:



The main goals of this effort were to optimize the conversion of  $Cl_2O$  to  $ClF_3O$  and to understand the fluorination process by which the conversion is effected. Several parameters were examined:  $Cl_2O$ -metal fluoride complex formation, fluorination temperature, sample size, reaction time, and product recovery temperature.

Because the addition of alkali metal fluorides to  $Cl_2O$  has been essential to  $ClF_3O$  synthesis, conditions leading to effective  $CsF-Cl_2O$  and  $KF-Cl_2O$  complexes were examined. Formation of the  $CsF-Cl_2O$  complex was complete at -80°C after 6 hours (disappearance of  $Cl_2O$  color), while at -22°C,  $Cl_2O$  vapor in contact with excess  $CsF$  was only one-third complexed after 11 hours. This observation was attributed to enhanced solid/liquid

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contact at -78 C. Once formed, the CsF complex was stable to dissociation at -22 C but showed a pressure of at least 6 mm Hg at 0 C. The potassium fluoride complex, however, formed only slowly at -80 C and was not stable at -45 C. The optimum temperature for fluorination was considered the maximum temperature at which the  $\text{Cl}_2\text{O}$  complex is intact and reacts smoothly. A tabulation of  $\text{Cl}_2\text{O}$ -CsF fluorinations at several temperatures is presented in Table 5. Variations in the quantity of  $\text{Cl}_2\text{O}$  used and the reaction time were also examined. Only  $\text{ClF}_3\text{O}$  that was evolved at ambient temperature was considered in Table 5. Subsequent evidence for  $\text{ClF}_3\text{O}$ -CsF complex formation suggested that several low yields and variations in yield from run to run were due, in part at least, to  $\text{ClF}_3\text{O}$  containing solids which could be heated to give additional  $\text{ClF}_3\text{O}$ . Although no clear-cut correlations between yield and experimental parameters are evident, several satisfactory conversions to  $\text{ClF}_3\text{O}$  have been obtained after several days at Dry Ice temperature.

#### Solid Products From Fluorination of $\text{Cl}_2\text{O}$ -CsF Complexes

The low-temperature fluorination of the  $\text{Cl}_2\text{O}$ -CsF complex might be expected to yield complexes of  $\text{ClOClF}_2$ ,  $\text{ClF}_2\text{OClF}_2$ ,  $\text{ClF}_2\text{OClF}_4$ , and possibly  $\text{ClF}_4\text{OClF}_4$  as well as complexes of  $\text{ClF}$ ,  $\text{ClF}_3$ ,  $\text{FClO}_2$ , and  $\text{ClF}_3\text{O}$ . Products removed by pumping at ambient temperature were  $\text{FClO}_2$ ,  $\text{ClF}_3\text{O}$ , and occasionally  $\text{ClF}_3$ . Pyrolysis of the remaining solid products yielded additional  $\text{ClF}_3\text{O}$  as well as  $\text{ClF}$  and an unknown species. The unknown partially passed through a -160 C trap and showed infrared absorptions in the ClO and ClF regions. This new compound may be a new F, Cl, O compound. The products  $\text{ClF}_3\text{O}$  and  $\text{ClF}_3$  could have arisen from either degradation of  $\text{ClF}_4\text{OClF}_2\text{-CsF}$  or from  $\text{Cs}^+\text{ClF}_4\text{O}^-$  and  $\text{Cs}^+\text{ClF}_4$ . Chlorine monofluoride and any new F, Cl, O species could similarly have arisen from either their CsF complexes or CsF complexes of the fluorinated  $\text{Cl}_2\text{O}$  structure.

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TABLE 5

CONVERSION OF CsF - Cl<sub>2</sub>O COMPLEX TO ClF<sub>3</sub>O

Temperature, C	Time		Cl <sub>2</sub> O Used, millimoles	Yield, percent
	Days	Hours		
0		0.5	8.7	0
		1	13	11
		2	15	0
		3	6.1	62
-22		2.5	32	11
		3	13	10
		3	24	26
		4	11	22
-45		9.5	32	46
-78		3.5	3.9	82
		6	11	79
		8	5.2	22
		9	11	21
		10	3.6	26
		10	333	2.4
		11	129	76
		12	1.1	11
		13	5.2	22
		13	8.6	41
		19	75	14
		20	35	3.2
		22	8.6	5.1
		26	7.8	43

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## Chemical Studies of $\text{ClF}_3\text{O}$

The chemistry of  $\text{ClF}_3\text{O}$  was expected to parallel that of  $\text{ClF}_3$  with regard to its behavior with strong Lewis acid and bases. That is, reactions involving either the addition or loss of fluoride were considered likely. Oxydation reactions involving the loss of two fluorine atoms are also considered possible, although less likely.

1-Base Reactions. The pentavalent ion  $\text{ClF}_4\text{O}^-$  was initially sought using  $\text{FNO}$  as a donor:



Considering the predicted enhanced acidity of  $\text{ClF}_3\text{O}$  over that of  $\text{ClF}_5$ , there is a high expectation of preparing the complexes  $\text{NO}_2^+\text{ClF}_4\text{O}^-$  and  $\text{NO}_3^-\text{ClF}_4\text{O}^-$ . Two reactions were carried out using  $\text{FNO}$  and  $\text{ClF}_3\text{O}$ . No conclusions could be drawn inasmuch as hydrogen nitrate was observed as a product, signifying an air leak in the system. A mixture of  $\text{FNO}_2$  and  $\text{ClF}_3\text{O}$  showed a marked vapor pressure decrease indicating complex formation. Experiments to more completely define the complexes of  $\text{ClF}_3\text{O}$  with  $\text{FNO}$  and  $\text{FNO}_2$  are now in progress.

Evolution of  $\text{ClF}_3\text{O}$  from  $\text{CaF}$ -containing solids was achieved by pyrolysis and suggested the presence of the salt  $\text{Ca}^+\text{ClF}_4\text{O}^-$ . The complex  $\text{CaF} \cdot \text{ClF}_3\text{O}$  was formulated as  $\text{Ca}^+\text{ClF}_4\text{O}^-$  by virtue of its relative thermal stability in analogy with other alkali metal fluoride-interhalogen fluoride salts (1, 2 and 5). This salt represents the first example of a stable pentavalent fluorinated chloro-centro anion. Previous work with  $\text{CaF}$  and  $\text{ClF}_3\text{O}$

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gave little indication of complex formation at -80°C, an observation which may have been due to solidification of  $\text{ClF}_3\text{O}$  at -66°C before sufficient contact with CsF was achieved. While the formation of the  $\text{CsF}\cdot\text{ClF}_3\text{O}$  complex in situ was established during the course of the reaction of  $\text{ClONO}_2$ , it was not known whether it could be produced directly from  $\text{ClF}_3\text{O}$  and CsF. Exposure of  $\text{ClF}_3\text{O}$  to fused and freshly powdered CsF at ambient temperature overnight resulted in only small amounts of  $\text{ClF}_3\text{O}$  remaining in the gas phase. Pyrolysis of the residual solids led to the evolution of  $\text{ClF}_3\text{O}$  of good purity, demonstrating the reversible reaction:



Separation of  $\text{ClF}_3\text{O}$  from  $\text{ClF}_3$  and  $\text{FClO}_2$ , the usual contaminants, was attempted with  $\text{BF}_3$  in the hope that  $\text{ClF}_3\text{O}$  would be a weaker Lewis base than either impurity. A sample of impure  $\text{ClF}_3\text{O}$  was treated with a lesser volume of  $\text{BF}_3$  for 20 minutes at -80°C.  $\text{ClF}_3$ ,  $\text{FClO}_2$ , and excess  $\text{ClF}_3\text{O}$  were volatile at this temperature, but  $\text{BF}_3$  was not. No additional pressure was observed at room temperature indicating the absence of  $\text{ClF}_2^+\text{BF}_4^-$  and  $\text{ClO}_2^+\text{BF}_4^-$  in the remaining solids.

Oxychlorine trifluoride exhibited a relatively strong basic behavior and reacted preferentially while most if not all of the  $\text{FClO}_2$  and  $\text{ClF}_3$  remained free. The  $\text{BF}_3$  complex of  $\text{ClF}_3\text{O}$  is a white solid which can be sublimed only slowly at 100°C and  $10^{-3}$  mm Hg.

The reaction of  $\text{ClF}_3\text{O}$  as a Lewis base toward  $\text{AsF}_5$  resulted in the formation of a white solid, nonvolatile at 50°C. Such a complex was expected to be  $\text{ClF}_2\text{O}^+\text{AsF}_6^-$ . However, it was not determined whether a side reaction may have occurred to give  $\text{ClO}_2^+\text{AsF}_6^-$ , which behaves similarly (Ref. 1).

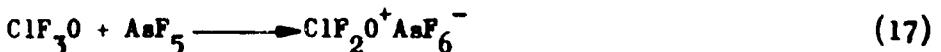
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Oxychlorine trifluoride therefore exhibits a pronounced amphoteric character similar to chlorine trifluoride, reacting both as an acid and a base (Eq. 14):

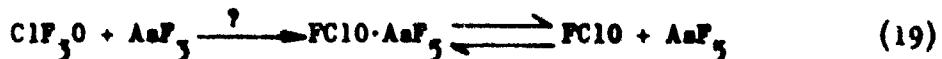


Reaction of  $\text{ClF}_3^0$  and  $\text{F}_2$ . A series of fluorination experiments in the same Monel reactor with different samples of  $\text{ClF}_3^0$  was conducted consecutively in hopes of forming  $\text{ClF}_5^0$ . Five runs from 70 to 284°C yielded no new species. Fluorination of fluorinated  $\text{Cl}_2^0$ -metal fluoride complexes at various temperatures as a possible route to  $\text{ClF}_5^0$  are in progress.

Reaction of  $\text{ClF}_3^0$  and  $\text{N}_2\text{F}_4$ . The reaction of  $\text{ClF}_3^0$  with  $\text{N}_2\text{F}_4$  was examined as a possible route to  $\text{FC10}$  as in the following equation:



The vapor or gas pressures of the system  $\text{ClF}_3^0\text{-N}_2\text{F}_4$  showed no appreciable deviations from calculated pressures over the temperature range -80 to 60°C. Under the conditions used,  $\text{ClF}_3^0$  was compatible with  $\text{N}_2\text{F}_4$ ; i.e., no reaction was observed. There is a good possibility of arriving at  $\text{FC10}$  by the alternate fluorination of  $\text{AsF}_5$  owing to the additional driving force of complex formation:



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## MISCELLANEOUS REACTIONS

### Attempted Synthesis of $\text{NF}_2\text{ONF}_2$

During the recent investigations of reactions of the  $\text{INF}_2\text{-KF}$  complex and  $\text{OF}_2$ , nonreproducible infrared indications for a new compound, possibly  $\text{NF}_2\text{ONF}_2$ , were obtained. An alternate route to  $\text{NF}_2\text{ONF}_2$ , namely the reaction of  $\text{Cl}_2\text{O}$  and  $\text{N}_2\text{F}_4$ , was examined at  $-112^\circ\text{C}$  in Pyrex. When an excess of  $\text{N}_2\text{F}_4$  was used, the products were  $\text{FNO}$ ,  $\text{ClNF}_2$ , and  $\text{Cl}_2$ ; when  $\text{Cl}_2\text{O}$  was in excess,  $\text{ClONO}_2$ ,  $\text{ClO}_2$ , and  $\text{Cl}_2$  were found. Solids believed to be  $(\text{NO})_2\text{SiF}_6$  were observed in each case. No further studies are planned in this direction.

### Reactions of Fluorine Perchlorate

The synthesis of the  $\text{BrF}_6^+$  cation was attempted to provide a model for the  $\text{ClF}_6^+$  cation. Bromine pentafluoride and fluorine perchlorate were combined in hopes of forming hexafluorobromine (VII) perchlorate:



The only detectable reaction was a 10-percent decomposition of  $\text{FOClO}_3$  to  $\text{FOClO}_3$  and noncondensable gas.

### Synthesis of New Br, F, O Compounds by Fluorination of $\text{Br}_2\text{O}$

Samples of  $\text{Br}_2\text{O}$  were prepared from yellow  $\text{HgO}$  and bromine in Freon 11 at  $-45$  to  $-80^\circ\text{C}$ . The formation of  $\text{Br}_2\text{O}$  was deduced on the basis of the same

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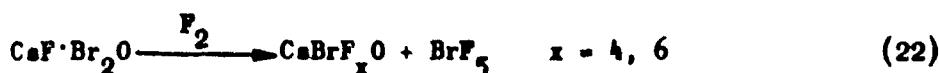
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meager information that is in the literature (Ref. 6). This included the black color, low volatility, and decomposition of the sample above -40°C giving bromine and noncondensable gas (oxygen).

The CsF complex of this material was formed from the Freon 11 solution at low temperature. After removing the solvent, the complex was fluorinated with the expectation of forming  $\text{BrF}_3\text{O}$  and/or  $\text{BrF}_5\text{O}$ . After several days, the reaction yielded room temperature volatile gases composed of  $\text{BrF}_5$  with lesser amounts of  $\text{FNO}_2$ ,  $\text{SOF}_2$ , and  $\text{SF}_6$ . In addition, several weak, unidentified absorptions were present in the infrared spectrum of the mixture. Too little sample was obtained to permit isolation of the components producing these absorptions. The CsF used in this reaction had become a fused mass, which on hydrolysis gave large amounts of  $\text{Br}_2$  vapor. In view of more recent Rocketdyne findings regarding the course of the  $\text{Cl}_2\text{O}\cdot\text{CsF}$  fluorinations, wherein it was observed that some of the  $\text{ClF}_3\text{O}$  formed remained in the reactor as a stable complex, it is probable that  $\text{BrF}_3\text{O}$  or possibly  $\text{BrF}_5\text{O}$  would be similarly complexed with CsF. Pyrolysis of the solids from the  $\text{Br}_2\text{O}\cdot\text{CsF}$  fluorination is in progress to free any complexed F, Br, O species.



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**EXPERIMENTAL EFFORT**

**PREPARATION OF  $\text{Cl}_2\text{O}$**

Yellow  $\text{HgO}$  was freshly prepared by the reaction of mercuric chloride and sodium hydroxide solutions. After drying and powdering,  $\text{HgO}$  was loaded into small glass ampoules together with appropriate amounts of chlorine. The closed, evacuated ampoule was kept at Dry Ice temperature at least overnight, although longer reaction periods were beneficial rather than detrimental to  $\text{Cl}_2\text{O}$  formation. Very pure  $\text{Cl}_2\text{O}$  was obtained if  $\text{HgO}$  was in excess, while better utilization of the oxygen of  $\text{HgO}$  was achieved if chlorine was in excess. Impure  $\text{Cl}_2\text{O}$  was upgraded by trap-to-trap distillation using carbon disulfide slush (-112°C) and liquid nitrogen baths. The purity and identity of the product was established by its infrared spectrum (Ref. 7), vapor phase chromatography and vapor pressure.

**PREPARATION OF  $\text{Br}_2\text{O}$**

The synthesis of  $\text{Br}_2\text{O}$  was accomplished in much the same manner as that of  $\text{Cl}_2\text{O}$ . The reactants  $\text{Br}_2$  and  $\text{HgO}$  were mixed in Freon 11 solvent to provide contact while maintaining low temperatures. The reaction was conducted over several days at -45 to -80°C with occasional agitation. Bromine monoxide was obtained in reasonably good purity by subsequent vacuum fractionation. Usually this was not necessary as the  $\text{Br}_2\text{O}$ -Freon 11 solution was used to form the  $\text{Br}_2\text{O}\cdot\text{CaF}$  complex directly. The bromine and Freon 11 were then stripped off.

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### PREPARATION OF $\text{ClNO}_3$

Chlorine nitrate was prepared by allowing roughly equimolar quantities of  $\text{Cl}_2\text{O}$  and  $\text{N}_2\text{O}_4$  or  $\text{N}_2\text{O}_5$  to react in evacuated glass ampoules at -80°C overnight or longer. Residual  $\text{Cl}_2\text{O}$  indicated by its red color was consumed by allowing the reaction to proceed briefly in the vacuum line at ambient temperature. The  $\text{ClNO}_3$  produced was purified by vacuum fractionation and identified by its infrared spectrum (Ref. 8) and vapor pressure (Ref. 9).

### FLUORINATION OF HYPOHALITE-ALKALI METAL FLUORIDE COMPLEXES

Regardless of the material being fluorinated, before the introduction of fluorine into the metal cylinder, at least 16 hours were allowed to perform the complex substrate, usually at -80°C. After cooling to -196°C, a twenty-fold molar excess of fluorine was condensed into the cylinder. The reactor temperature was generally maintained at -80°C for several days before removing the excess fluorine at -196°C. Volatile products were then separated, trapped, and examined.

### PREPARATION OF OXYCHLORINE TRIFLUORIDE

Oxychlorine trifluoride was prepared by the fluorination of an alkali metal- $\text{Cl}_2\text{O}$  complex. In a typical preparation the alkali-metal fluoride was first dried by fusion and then transferred to a dry box for grinding. The powdered fluoride was placed in a 300-milliliter stainless-steel cylinder. Chlorine monoxide was distilled into the reactor in vacuo. The cylinder was maintained at -78°C at least overnight to allow complex

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formation. Then fluorine was added and allowed to warm to the desired reactor temperature. After reaction, the products which were volatile at ambient temperature were separated by fractionation using a -95 C slush bath which condensed most of the  $\text{ClF}_3\text{O}$ . Any unreacted  $\text{Cl}_2\text{O}$ , other products, and impurities passed through. Additional  $\text{ClF}_3\text{O}$  was evolved by heating the residual solid in the reactor with a heat gun.

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1 ORIGINATING ACTIVITY (Corporate author)		2a REPORT SECURITY CLASSIFICATION
Rocketdyne, a Division of North American Aviation, Inc., 6633 Canoga Avenue, Canoga Park, California		CONFIDENTIAL
3 REPORT TITLE		
Inorganic Halogen Oxidizers		
4 DESCRIPTIVE NOTES (Type of report and inclusive dates)		
Quarterly Report (29 May 1965 through 28 August 1965)		
5 AUTHOR(S) (Last name, first name, initial)		
Pilipovich, D., Lindahl, C. B., Bauer, H. F., Schack, C. J.		
6 REPORT DATE 30 September 1965		7a TOTAL NO OF PAGES 28
7b NO OF REPS 9		
8a CONTRACT OR GRANT NO. Nonr 4428(00)		8b ORIGINATOR'S REPORT NUMBER(S) R-5883-4
8c PROJECT NO ARPA Order No. 23		8d OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
10 AVAILABILITY/LIMITATION NOTICES		
11 SUPPLEMENTARY NOTES		12 SPONSORING MILITARY ACTIVITY Advanced Research Projects Agency Washington 25, D.C.
13 ABSTRACT		
<p>The new oxidizer oxychlorine trifluoride, <math>\text{ClF}_3\text{O}</math>, has been prepared by the fluorination of cesium fluoride complexes of both chlorine monoxide and chlorine nitrate. The density of <math>\text{ClF}_3\text{O}</math> is <math>1.90 \pm 0.05 \text{ g/cc}</math> at <math>25.5^\circ\text{C}</math>; it melts at <math>-66^\circ\text{C}</math> and boils at <math>29.4^\circ\text{C}</math>. The vapor pressure/temperature equation for <math>\text{ClF}_3\text{O}</math> has been obtained from <math>-22</math> to <math>32^\circ\text{C}</math>: <math>\log_{10}P \text{ (mm)} = 8.433 - 1680/T</math>. The molar heat of vaporization is <math>7.7 \text{ kcal}</math>. Oxychlorine trifluoride was found to be thermally stable to <math>284^\circ\text{C}</math>, although reactivity with metal containers was noted. Elemental analyses confirm the empirical formula <math>\text{ClF}_3\text{O}</math>. Several members of a new class of complexes have been formed: <math>\text{Cl}_2\text{O}\cdot\text{CaF}</math>, <math>\text{Br}_2\text{O}\cdot\text{CaF}</math>, and <math>\text{Cl}_2\text{NO}_2\cdot\text{CaF}</math>. Fluorination of these materials has led to solid oxyhalogen fluoride complexes. Evidence for another new oxychlorine fluoride candidate has been obtained during this study. Reactions of <math>\text{ClF}_3\text{O}</math> with Lewis acids and bases gave the complexes <math>\text{NO}_2^+\text{ClF}_4\text{O}^-</math>, <math>\text{Ca}^+\text{ClF}_4\text{O}^-</math>, <math>\text{ClF}_2\text{O}^+\text{HF}_4^-</math>, and <math>\text{ClF}_2\text{O}^+\text{AsF}_6^-</math>, indicating a pronounced amphoteric behavior. No reaction of <math>\text{ClF}_3\text{O}</math> was observed with either <math>\text{F}_2</math> or <math>\text{N}_2\text{F}_4</math>. A new, convenient synthesis of <math>\text{Cl}_2\text{O}</math> has yielded a product of improved purity. The reaction of <math>\text{BrF}_3</math> with <math>\text{POCl}_3</math> failed to give <math>\text{BrF}_6^+\text{ClO}_4^-</math> while the reaction of <math>\text{Cl}_2\text{O}</math> and <math>\text{N}_2\text{F}_4</math> gave no new products. (C)</p>		

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14. <b>KEY WORDS:</b> Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical content. The assignment of links, rules, and weights is optional.							

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